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CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-743

FORMULATION OF A BROAD-SPECTRUM, ALL-WEATHER, SOLID-BASED, PERACETATE - "SOLVENT" DRY DECONTAMINANT CONCENTRATE

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In a joint project, the U.S. Army Edgewood Chemical Biological Center (ECBC) and Naval Service Warfare Center-Dahlgren Division combined ECBC's Decon Green® technology with Dahlgren Decon's microemulsion-based solid peracetyl borate formulation expertise to develop a broad-spectrum, easy-to-mix, all-solid, CB, dry decontaminant concentrate (DDC) requiring only water for its reconstitution, and use at temperatures above freezing. The same DDC composition is also suitable for use below freezing down to -35 °C (-31 °F) via its dissolution in a purposely designed, antifreeze-solvent-water mixture, "cold-weather kit". Development of this DDC restores the capability for all-weather decontamination formerly provided by the discontinued DS2 decontaminant, while providing the additional capability for biological agent decontamination-an attribute historically lacking in DS2.

15. SUBJECT TERMS

Decon green	Decontamination	Decon concentrate	Peracetyl borate
Anthrax	VX	HD	GD

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PREFACE

The work described in this report was authorized under Project No. BA06DEC052. The work was started in February 2006 and completed in March 2008.

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FORMULATION OF A BROAD-SPECTRUM, ALL-WEATHER, SOLID-BASED, PERACETATE - "SOLVENT" DRY DECONTAMINANT CONCENTRATE

1.   INTRODUCTION

The U.S. Army Edgewood Chemical Biological Center (ECBC) and Naval Surface Warfare Center Dalhgren Division (NSWCDD) have been developing environmentally-friendly, peroxide-based decontaminants for the past several years. ECBC has developed Decon Green[®] [1-3], which uses aqueous hydrogen peroxide (H_2O_2) as its active ingredient for CB decontamination. Additionally, liquid non-ionic surfactants and penetrating solvents are used to provide facile dissolution of agents and surface decontamination that is superior to that of DS2 and/or other decontaminants on CARC-painted surfaces.[1] Indeed, Decon Green[®] was recently rated the best current decon technology to replace DS2 and STB for exterior-vehicle decontamination.[4] NSWCDD has been developing microemulsion-based CB decontaminant formulations (Dahlgren Decon) using solid peracetyl borate (PAB)—a potent sporicide—as its active ingredient.[5] Thus, it was desired to combine the two technologies to create an optimum, solid-based formulation.

        Goals of the Study

The goal of this endeavor was to develop an all-solid, dry decontaminant concentrate (DDC) that possesses reduced-weight (compared to all-liquid decontaminants); affords superior efficacy for chemical and biological (CB) agents; requires only water for its reconstitution; is fast and easy to mix, and is usable in all-weather conditions, down to $-32\,°C/-26\,°F$.[6]

2.   RESULTS

2.1   "Solvent" Selection

Owing to the desire for an all-solid formula, conventional liquid surfactants and solvents used in previous peroxide-based decontaminants[7-11] (i.e., Triton[®] X-100 (non-ionic surfactant) and propylene carbonate [PC]) could not be used. However, there are several commercial varieties of solid non-ionic surfactants available. Further, a "solvent" quite similar to propylene carbonate is ethylene carbonate (EC), a glassy-solid at room temperature. EC is water-soluble like PC and, with its similar structure, is similarly expected to be a good co-solvent and provide good penetrating properties for efficacious surface decontamination. Both of these items—surfactant and co-solvent—are primarily required to allow dissolution of water-insoluble HD. Thus, initial efforts centered on the ability of solid ionic surfactants and/or solid ethylene carbonate to solubilize this agent and/or its simulant 2-chloroethyl phenyl sulfide (CEPS).

Several solid non-ionic surfactants were examined for study, including Brij[®] 700, Igepal[®] DM-970 and Triton[®] X-405. Many of these solids are quite similar in structure to liquid

ionic surfactants except for their longer polyoxyethylene (POE) "head-groups". For example, Triton[®] X-405 possesses a 40-POE unit chain compared to only 10-POE for Triton[®] X-100. Although both surfactants possess the same isooctylphenyl ether hydrophobic "tail", the melting point of the former is elevated to near 50 °C, whereas the latter is only 6 °C. Thus, non-ionic surfactants, which will remain as free-flowing powders at potential elevated storage temperatures (not melt into hard-to-mix clumps), are easily achievable with sufficiently-long POE chains.

All the surfactants were able to dissolve HD and/or CEPS, but ultimately Triton[®] X-405 was selected for use owing to its better salt tolerance, which enables it to not phase-separate in the presence of peroxygen compounds, buffers, and activators. Furthermore, Triton[®] X-100 is widely used in agriculture applications and is biodegradable. Thus, Triton[®] X-405, with its similar head/tail-groups, is reasonably expected to be equally environmentally-friendly. Triton[®] X-405, alone, without EC co-solvent, is able to dissolve HD. Therefore, a co-solvent is not strictly required for dissolution of HD, thus saving additional weight in the final formula.

A penetrating co-solvent improves surface decontamination efficacy. However, even though solid EC "solvent" is very effective at penetrating CARC paint to allow for very a efficacious decontamination (see below), it is problematic in that it readily undergoes hydrolysis to toxic ethylene glycol (the "toxic" antifreeze)* under the basic conditions typically found in peroxide-based decontaminants.[1-3,7-11] Thus, for this reason, it was decided to remove EC from the DDC formulation. It should be noted here that PC is included in the "cold-weather kit" to assist surface-penetration under freezing conditions. Further, DDC development relied solely on the Triton[®] X-405 surfactant to dissolve HD for reaction and decontamination.

2.2 Solid Peroxygen Compound Selection

2.2.1 Considerations and Concerns

As stated above, one aim of the study was to use the potent sporicide PAB as the active ingredient. However, initial studies showed it to be problematic in that it tended to over-oxidize HD to its vesicant sulfone.[7] Moreover, it was not very effective against GD and rather massive quantities were required for VX. Thus, it was decided to use only the minimum amount of PAB required to provide for adequate bio decontamination and to select a second peroxygen compound to enable suitable chemical agent decontamination.

Early indications (personal communication with Mark Tucker, Sandia National Laboratory) suggested sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$, SPC) as an attractive candidate. However, at least three problems were discovered for practical use of SPC for decontamination. The first is that it generates solutions, which are too basic (ca. pH 10), thus, necessitating additional neutralization that could result in excessive heating and foaming when done on a large scale. The second problem is that rather large quantities are needed for VX, resulting in solutions of such high sodium content that it is difficult to keep surfactants in solution. The third difficulty is that it is extremely problematic to dissolve, requiring excessive stirring and dissolution time to get it into solution. Finally, it was eventually found that SPC is

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*Propylene carbonate similarly undergoes hydrolysis, but forms non-toxic propylene glycol (the "non-toxic" antifreeze).

not sufficiently stable in storage—even exhibiting decomposition at room temperature (see below).

The problems mentioned above with SPC, however, are overcome, for the most part, by the use of peroxydone (PD), a polyvinyl pyrrolidinone-H_2O_2 complex.* As the H_2O_2 is polymer-bound in this material, no sodium or salt is generated following its dissolution. Moreover, its solutions are already near neutral pH, so only minor adjustment or buffering is required. Further, PD simply melts into solution upon contact with water, rendering it extremely quick and easy to dissolve. And to round out its ideal nature for use as a military decontaminant, PD is by far the most stable of any solid peroxygen compound (yet still considerably less stable than aqueous peroxide). Thus, PD was selected as the second solid-oxidant of choice, in addition to PAB, to formulate the DDC. Storage stability and anticipated shelf-lives of PD and PAB are discussed in Sections 2.3 and 2.4, respectively.

2.2.2   Peroxygen Compound Thermal Stabilities under Military Storage Conditions

Concurrent with this project, a second study[12] was ongoing to examine the relative stabilities of liquid and solid peroxygen compounds under military storage conditions.[13] Candidates included aqueous H_2O_2 and several solid peroxygen compounds. Although solid sodium perborate monohydrate (SPB) and urea peroxide (UP) were initially selected for study, Giddens et al.[14] found there was no readily-available source for SPB. Urea peroxide exhibits extremely-poor stability, even at room temperature; thus, not warranting further, high-temperature testing. Indeed, the MSDS[15] for UP recommends storage at 2 to 8 °C (36 to 46 °F). Therefore, for reasons of limited availability and poor thermal stability, SPB and UP, respectively, were judged unsuitable for military use. Thus, only the SPC, PD, and PAB solids remained in the study. The results for these materials are shown in Table 1. For comparison, representative data for 35% aqueous H_2O_2 is also included. All samples were packaged by STERIS Corporation (St. Louis, MO). according to industry best practices and standards.

Two additional samples, comprising oxidants PAB, SPC, and citric acid (CA, a buffer/activator), were also examined to determine the compatibility of mixtures of these oxidants and/or buffers/activators: Mixture #1 contained 14% PAB and 86% SPC, whereas Mixture #2 contained 12.6% PAB, 75.8% SPC, and 11.6% CA.

MIL-STD-810F, Method 501.4, calls for diurnal, temperature cycling from 33 to 49 °C (91 to 120 °F; "hot") and 33 to 71 °C (91 to 160 °F; "Induced Hot"). During storage under these conditions the concentrations of the peroxygen materials were assayed at pre-determined intervals. All results are expressed as weight percent H_2O_2 for convenience.**

Regarding the data in Table 1, it is readily apparent that the aqueous H_2O_2 lost no more than 1% after six weeks, whether at ambient or cycling the temperature to 49 or 71 °C. However, the solid peroxygen compounds did not fare nearly as well. The OCI SPC, for example, lost 2.2%

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* www.ispcorp.com/products/oralcare/index.html (accessed November 26, 2007).
**Strictly speaking, the active-oxygen in PAB is peracetic acid, $CH_3C(O)OOH$, not hydrogen peroxide, HOOH, but the AO content is still reported on the basis of the latter.

Table 1. H$_2$O$_2$/Peroxygen Compound Stabilities at Ambient and Up to 49 and 71 °C

Peroxygen Material	Initial			6 Weeks			% Decrease[a]		
	Ambient	49 °C	71 °C	Ambient	49 °C	71 °C	Ambient	49 °C	71 °C
FMC Std 35% H$_2$O$_2$	35.8	35.8	35.8	35.7	35.6	35.7	0.3	0.6	0.3
OCI Sodium Percarbonate	13.5	13.5	13.5	13.2	13.0	10.8	2.2	3.7	20.0
Solvay Sodium Percarbonate	14.6	14.6	14.6	13.1	12.5	10.2	10.3	14.4	30.0
ISP Peroxydone XL-10	16.9	16.9	16.9	17.0	17.0	15.3[b]	+0.6	+0.6	9.5
Sodium Peracetyl Borate (PAB)	5.4	5.4	5.4	5.5	5.4	4.6[b]	+1.9	0	15[b]
PAB/SPC Mixture (#1)	12.5	12.5	12.5	12.3	12.5	9.8	1.6	0	21.6
PAB/SPC/CA Mixture (#2)	11.4	11.4	11.4	11.1	10.9	5.0	2.7	4.5	56.1

[a] All values reflect a decrease in H$_2$O$_2$ concentration, except those designated with a "+" where an increase was observed (obviously within experimental error).
[b] 2 weeks at 71 °C.

after 6 weeks at *ambient* temperature, and 3.7 and 20.0% at 49 and 71 °C, respectively. The Solvay SPC performed even worse, losing an astounding 10.3% after only   6 weeks at *ambient* temperature, and 14.4 and 30.0% at 49 and 71 °C, respectively. Although PAB performed better than either SPC at ambient and 49 °C—suffering no loss after 6 weeks at either temperature—it did manage to lose 15% after only 2 weeks at 71 °C, placing it on par with SPC at the highest temperature. The behavior of PAB is entirely consistent with its known potential for self-accelerating decomposition above 50 °C.[16] Yet, by far, the best of the solids was PD, which, like PAB, suffered no loss after 6 weeks at either ambient or 49 °C and lost only 9.5% after 6 weeks at 71 °C. Thus, PD is selected as the best *solid* peroxygen material for military decontaminants (keeping in mind that aqueous H_2O_2 still affords the best stability).

Although not used in the final DDC formula (see below), it is worth pointing out for the mixtures that PAB/SPC compositions (#1) appeared to retain the stability of the individual oxidants (i.e., they seemed to be completely compatible with each other in a simple, physical mixture as losses were comparable to those observed for [less-stable] SPC alone). However, the addition of CA to the oxidants (#2) resulted in a noticeable decrease in stability with this mixture losing an unprecedented 56.1% after 6 weeks at 71 °C. Thus, although PAB and SPC appear to be compatible with each other, the mixture is not compatible with CA (and, presumably, other activators).

2.2.3   Peroxygen Material Storage Shelf-Life

The negligible degradation (<1%) found for the aqueous H_2O_2 during the 6 week stability testing was insufficient to predict its shelf-life. However, using a theoretical model for H_2O_2 decomposition, Giddens et al.[14] calculated the expected concentration of H_2O_2 remaining over a 5 year span at three different temperatures. Thus, these values can be used to provide a general idea of the expected long-term stability for a given storage temperature.

For defining a "shelf-life" (i.e., the period of time for which a H_2O_2 solution remains viable for decontamination), a 10% loss threshold was arbitrarily chosen. Thus, 35% H_2O_2 is still considered viable at 31.5%. Based on this criterion and the calculated loss data,[14] *calculated* shelf-lives for aqueous H_2O_2 are shown in Table 2.

For the solid peroxygen compounds, substantial degradation occurred for SPC at all temperatures during the 6 week stability study and all the solids degraded noticeably at the highest temperature. Thus, except for cases where negligible degradation (<0.1%) occurred at the lower temperatures, it is possible to project some shelf-lives for these materials at certain temperatures using the same 10% loss criteria as discussed above for aqueous H_2O_2. These *experimentally-derived* shelf lives for the solid H_2O_2/AO materials are also shown in Table 2.

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Table 2. Calculated Shelf-Lives for Aqueous H_2O_2 and Experimentally Derived
Shelf Lives for Solid Peroxygen Compounds

Material	Ambient 21 °C (72 °F)	Hot Up to 49 °C (120 °F)	Induced Hot Up to 71 °C (160 °F)
Aqueous H_2O_2	>5 years	2 to 3 years	1 year
Sodium Percarbonate	Up to 7 months	Up to 7 weeks	About 2 weeks
Peracetyl Borate	Insufficient degradation	Insufficient degradation	About 10 days
Peroxydone XL-10	Insufficient degradation	Insufficient degradation	About 6 weeks

The shelf lives merely serve to drive home the point highlighted above for the thermal stability data that aqueous H_2O_2 is immensely more stable than any of the solid peroxygen compounds. This is especially true at the highest, uncontrolled storage temperature (71 °C/160 °F) anticipated for military storage: 1 year for aqueous H_2O_2 vs. days to weeks for solid materials For ambient to slightly elevated temperatures, the shelf life of aqueous H_2O_2 is years compared to months for SPC.

2.3   Bio Efficacy of Solid Peroxygen Compounds

The bio efficacy of aqueous H_2O_2—with and without activators—has already been demonstrated by Decon Green[®], an EPA-registered sporicide.[2] However, examination of the bio efficacy of the solid peroxygen materials was in order. Results for relatively low levels of these materials (50 mg/mL) are shown in Table 3. Results obtained for HTH are also shown. It is readily apparent that a small amount of the peracetyl acid donor PAB is much more effective at killing anthrax spores—exhibiting a total, 7-log kill—than comparable amounts of the solid H_2O_2-containing materials PD (<1-log kill) or SPC (0-log kill); even HTH afforded only a 4-log kill.

Table 3. Decon of 10^7 Challenges of *Bacillus anthracis* Δ Sterne Spores

Decon (50 mg/mL)	Final [H_2O_2]	Log Kill
PD	0.85%	<1
SPC	0.7%	0
PAB	N/A	7
HTH	N/A	4

It should be noted, though, that the experiments shown in Table 3 were conducted with quite low concentrations of the solid materials, 50 mg/mL, resulting in very low H_2O_2 concentrations of <1% for the solid peroxides. Conversely, H_2O_2-based, sporicidal[2] Decon Green[®] contains a much higher H_2O_2 concentration of 10.5%; so, H_2O_2 concentrations

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significantly higher than 1% are apparently required for bio efficacy. Thus, the data in Table 3 serves primarily to demonstrate the impressive bio efficacy afforded by quite low levels of peracetic acid (derived from PAB) compared to H_2O_2. Additional studies examining higher concentrations of PD and SPC would be required to fully explore the bio efficacy afforded by these solid peroxides.

2.4   Packaging of Solid Peroxygen Materials and the DDC

The main sticking point for shipping peroxygen compounds—either solid or liquid—is their self decomposition over time to generate oxygen, and the need to vent the pent up oxygen—lest the container bulge and/or burst from built-up pressure. This is even more true for the less-thermally-stable solid peroxygen materials (see above), which would tend to generate oxygen at a much faster rate than aqueous H_2O_2. Typically, unvented containers are required on aircraft; thus, one mode for packaging H_2O_2 discussed by Giddens et al.[14] involves placing the primary, vented "inner" container into a sealed metal can or drum "outer" container. Of course, to prevent untimely rupture in transit, the inner container would ideally be sealed within the outer container just prior to flight. Moreover, for the same reason, the outer container would be unsealed upon off loading from the plane at its destination (time being of the essence). It is essential to stress that it is not "*if*" a sealed container of peroxygen material will burst but "*when*". The "*when*" should definitely not be when it is on the plane.

An alternative strategy (personal communication with Frank Fusiak, International Specialty Chemicals) to the bottle-in-can packaging method available for the solid materials (but not liquids*) is to simply pack them in a bucket or drum. Apparently, the seals on these containers fortuitously allow built-up pressure to escape while still meeting the spirit of the non-venting requirement. Such a packaging arrangement is envisioned for the DDC, where the bucket would contain separate packages of PD and PAB situated amongst a mixture of Triton® X-405 and buffer/activator powders. To mix, the bucket would be opened; the packets of PD and PAB would be opened and dumped into the bucket; and the prescribed amount of water (or cold-weather kit solution) would be added to the bucket and stirred.

2.5   Formulation Experiments

2.5.1   PAB Alone

2.5.1.1   Chem Agent Testing of PAB

PAB liberates peracetic acid, a powerful oxidant, when dissolved in water. It was determined that PAB (MW = 509.5 g/mol) at concentrations of about 0.1 M, with 10% Triton® X-100 surfactant, is able to quickly dissolve and fully-react with 1:50 HD (0.16 M) challenges to yield non-vesicant HD-sulfoxide[18] (HDO, Scheme 1). Greater amounts of PAB resulted in over-oxidation of HD to its vesicant HD-sulfone (HDO_2). Formation of HDO_2 is to be avoided during

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*Unfortunately, these slight-of-hand containers could not be used for aqueous H_2O_2 although such wayward seals
  may prevent undue leakage of powder, they certainly would not be liquid-tight.

decontamination as its vesicant-action is near that of HD itself.[17-18]   Confirmation studies conducted with 1:50 challenges of HD (0.16 M) and peracetic acid (PA) showed that 0.34 M PA generates 7.0% vesicant sulfone within 1 min and 30.1% after 16 min.

Scheme 1. HDO
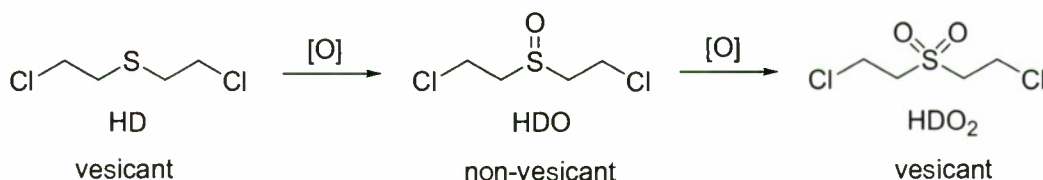
VX is less economical than HD towards oxidants as its cleaved thiol (RSH) side chain rapidly consumes copious oxidant and as it is oxidized to the corresponding sulfonic acid (RSO_3H, Scheme 2). Although it would appear that 1:50 challenges of VX (0.75 M) should require less oxidant than that needed to singly-oxidize HD to the non-vesicant sulfoxide, the oxidant-starved thiol group requires about 4.5 additional equivalents of oxidant, for a total of 5.5. Thus, the total amount of oxidant required by VX is about 4.1 M—more than enough to fully oxidize HD to the vesicant sulfone. Experiments with a 1:50 challenge of VX confirmed this expectation: a 0.1 M PAB/10% Triton® X-100 solution leaves about 63% VX unreacted.

Scheme 2. RSO_3H
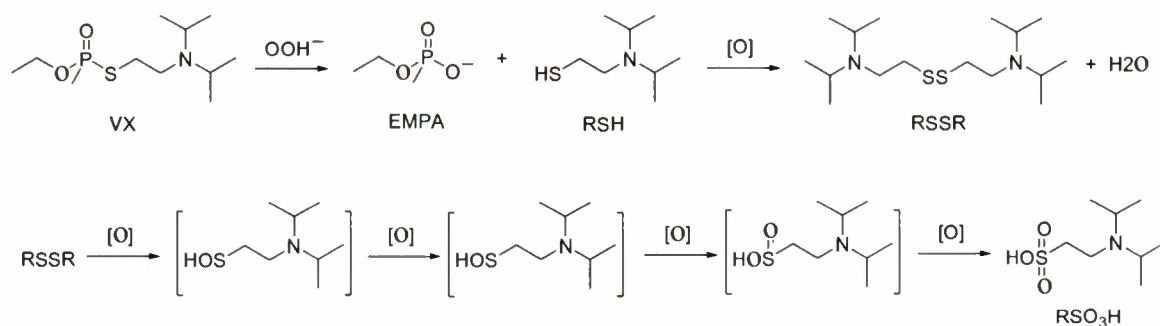
Attempts at reacting 1:50 challenges of GD with 0.1 M PAB/10% Triton® X-100 solution resulted in 74.6% GD remaining after 15 min. Significantly, however, two peroxy-pinacolyl methylphosphonate (pPMPA) species are evidently detected. Such a species is indicative of perhydrolysis by OOH^-.[7,19] As PAB is known to contain residual H_2O_2, the two peroxy species are assigned to normal pPMPA and peracetoxy-PMPA (paPMPA, PMPA-OOC(O)CH₃, Scheme 3). Thus, it appears that GD reaction with PAB occurs primarily via perhydrolysis with background OOH^- and $CH_3C(O)OO^-$. Further, note that the peroxy-PMPA intermediates consume an additional equivalent of oxidant upon decomposition to the final PMPA product.[19]

Scheme 3. paPMPA, PMPA-OOC(O)CH$_3$
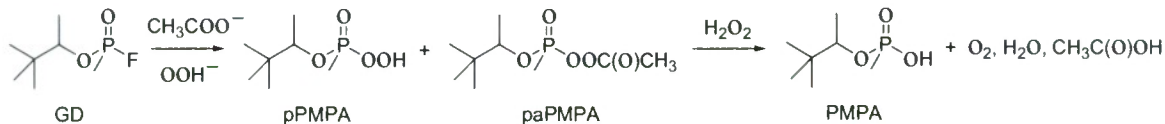
It was clear from these experiments and considerations that the DDC could not be formulated using PAB alone if vesicant HD sulfone was to be avoided, while achieving complete reactions with 1:50 challenges of VX and GD. Therefore, a second, more selective oxidant is needed. At this early point in the study, without benefit of any stability data for solid peroxygen compounds (see above), SPC was considered for this role.

2.5.1.2   Bio Agent Testing of PAB

PAB was tested* at 50, 40, 30, 20, 10, 5, and 0 (control) mg/mL with 5% Triton® X-405 in water. Exposing 1×10^7 challenges of *B. anthracis* Δ Sterne spores to these solutions in a conical tube for 15 min showed consistent 7-log reduction in spore count (100% kill) for 20 mg/mL PAB over three replicates on two separate days (six data sets). Therefore, a concentration of 20 mg/mL PAB was selected as the minimum concentration required for adequate bio decon performance.

This concentration of PAB (with 5% Triton® X-405) was examined for its effectiveness on six material surfaces containing 1×10^7 challenges of *B. anthracis* Δ Sterne spores: polycarbonate, glass, steel, AF topcoat paint, CARC, and butyl rubber. A 15-min decon period was also used. The results are shown in Figure 1.

It can be seen by the data in Figure 1 that the solution is less effective for spores on surfaces than in suspension. This observation is typical as reduced efficacy is often observed for decontaminants on material surfaces. This is especially true for rubber, which has historically proven to be a particularly recalcitrant surface for spore-decontamination.

2.5.2   PAB/SPC Mixtures

SPC liberates H$_2$O$_2$ when dissolved in water, which selectively oxidizes HD to the non-vesicant sulfoxide. Thus, its combination with minimum amounts of PAB can provide for additional VX capacity, while avoiding undue HD-sulfone formation.

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*Wells, C.; Shegogue, D.; Delgado, J.; McPherson, D.; Hooban, C.; Sobota, A.; Sobota, L. *Single Tube Method (STM) for Testing the Decontamination Efficacy of a Peracetate Solvent Against B. Subtilis and B. Anthracis Δ Sterne Spores Inoculated on Large Coupons*; NSWCDD: Dahlgren, VA; unpublished data, May 2010.

Initial studies* conducted with SPC alone showed that 0.5 M SPC generates a pH >10 solution, which does react with 1:50 challenges of VX within 15 min. However, such a high pH is undesirable for a decontaminant owing to both materials compatibility concerns and overall stability (pot-life) of the mixed decontaminant. Using citric acid to adjust a 0.5 M SPC solution to about pH 8 resulted in <50% VX reaction within 15 min. However, 2.0 M SPC adjusted to pH 9 reacted completely with VX within only 5 min. Thus, it is possible to achieve quick, complete reactivity at more moderate pH, but quite large amounts of SPC are required.
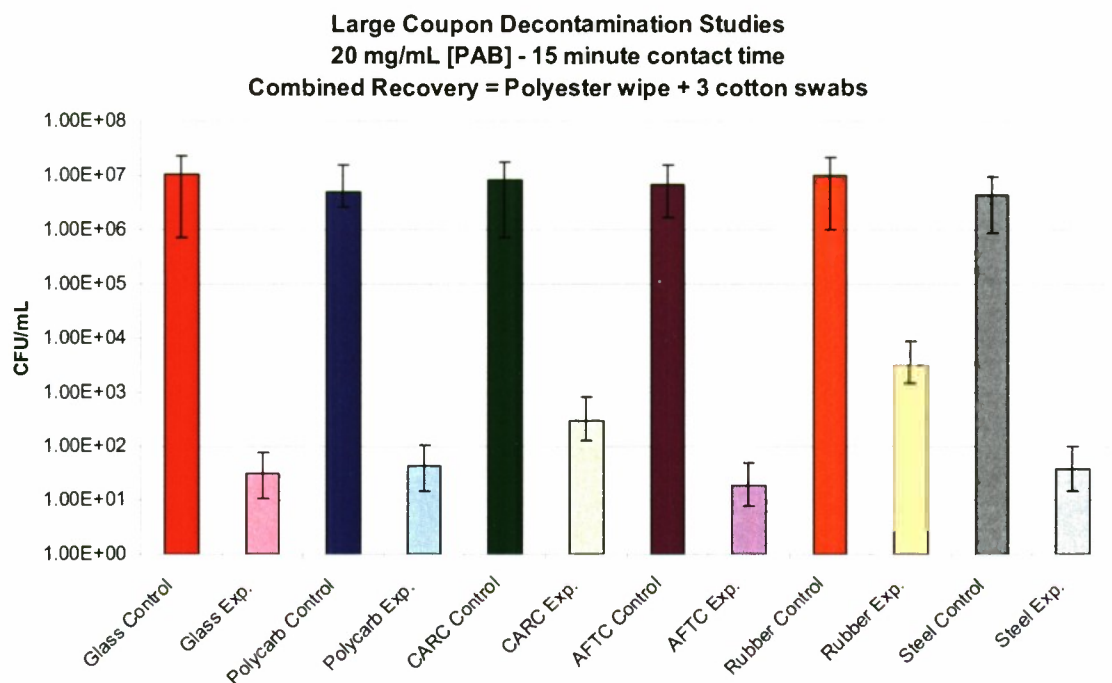
Figure 1. Efficacy of 20 mg/mL PAB – 5% Triton® X-405 Solutions against 1×10^7 Challenges of *B. anthracis* Δ Sterne Spores on Various Surfaces

Moving on to PAB/SPC mixtures and 1:150 challenges of VX, 0.1 M PAB and 0.5 M SPC yielded pH 9 (without citric acid) and resulted in 53.0% VX remaining after 15 min; but with 0.5 M SPC and 0.05 M PAB (pH 10) only 5.6% VX remained. PAB apparently only lowers the pH of SPC solutions, retarding the activity; it does not enhance SPC reactivity for VX.

Attempts at using such high SPC/PAB concentrations with surfactants resulted in many of the surfactants discussed above "salting-out" of solution. Although adding propylene glycol (PG) as a co-surfactant enabled maintaining surfactant in such high salt-content solutions, such an ingredient (liquid) defeats the purpose of an all solid DDC. However, one surfactant, Triton® X-405, did not salt-out, even without PG as a co-surfactant. Thus, this particular surfactant, alone, was chosen for further development work.

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*1:50 challenges of agent to decontaminant were used. HD reactions were rapidly stirred in glass vials, sampled, and analyzed by NMR.[7] VX and GD reactions were observed in situ by NMR.[7]

2.5.3 PAB/SPC Mixtures with Ethylene Carbonate

Panel tests were conducted to determine the efficacy of solid ethylene carbonate (EC) as a penetrant additive for decontamination of HD on CARC painted surfaces. The results are shown in Table 4. Also indicated at the bottom of the table is the Required Operational Contact Hazard Level of 10 $\mu g/cm^2$ (100 mg/m^2).[6]

It is clear that the Triton[®] X-405 surfactant and EC improve HD-decontamination efficacy on CARC paint. Separate testing of 10, 20, and 30% EC aqueous solutions in contact with CARC paint for 24 h found no observable softening, yet EC provided quite remarkable decontamination performance, effectively reducing the residual HD to within the vicinity of the Required Operational Contact Hazard Level of 10 $\mu g/cm^2$.[6] Considering that these panel tests were conducted by extraction ($CHCl_3$) to recover all residual HD left, the actual contact hazard levels would most likely have been considerably <10 $\mu g/cm^2$ for the 25 and 30% EC formulas. However, as discussed above, EC undergoes hydrolysis to toxic ethylene glycol at the pH required for H_2O_2-based decontaminants to provide GD and VX reactivity. Thus, EC was dropped from further consideration for inclusion in the DDC.

Additional tests were performed with Triton[®] X-405, alone, without EC. These results are shown in Table 5. The base solutions for these trials, containing only 0.1 M PAB and no SPC, tended to perform better than those above. This can be rationalized by assuming that the solutions with lower salt content were able to more quickly solubilize and react with HD. Further note that surfactant levels beyond 1% or so did not afford any significant improvement in surface decon efficacy; thus, only low-levels of Triton[®] X-405 are required; an additional weight savings in the DDC formulation.

Although PAB/SPC mixtures could easily be made effective against 1:50 HD, the amount of SPC required for VX still resulted in problems with salting-out the surfactant. Furthermore, results of stability tests had finally revealed that SPC really was not stable in storage, even at room temperature. However, these results did unveil the better stability of Peroxydone, which contains no salt whatsoever. Thus, it was decided to use this oxidant instead of SPC.

2.5.4 Peroxydone/PAB Mixtures

2.5.4.1 Chem Agent Testing

The polyvinylpyrrolidinone component of Peroxydone (PD) did not appear to assist in solubilizing HD, so Triton[®] X-405 was still required for this oxidant. PD solutions could be activated with K_2MoO_4 to yield peroxomolydate species (which enhances HD oxidation) as previously seen for aqueous H_2O_2.[8] Furthermore, PD solutions could be made basic to enable complete reactions with 1:50 challenges of VX and GD, while avoiding the high salt problem of SPC. Finally, very good efficacy could be obtained for HD on CARC paint as shown in Table 6. Note that efficacy tended to increase up to 10% Triton[®] X-405, but further amounts of the surfactant had little effect. The two runs done for 10% Triton[®] X-405 show how

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irreproducible panel test results can be from day-to-day, thus, the importance of running control experiments to allow for the meaningful comparison of different data sets.

Table 4. Effect of Surfactant and Ethylene Carbonate (EC) Penetrant on Decontamination of HD on CARC Painted Panels[a]

Decon	Total HD Remaining ($\mu g/cm^2$)	% Decon
No EC/No Triton[®] X-405[b,d]	332.27	66.8
No EC/5% Triton[®] X-405[b,d]	215.70	78.4
No EC/1% Triton[®] X-405[c,e]	318	68.2
5% EC/1% Triton[®] X-405[c,e]	287	71.3
15% EC/1% Triton[®] X-405[c,e]	146	85.4
20% EC/1% Triton[®] X-405[c,e]	88	91.2
25% EC/1% Triton[®] X-405[c,e]	14	98.6
30% EC/1% Triton[®] X-405[c,e]	33	96.7
Required Operational Level	10	99.0

[a] Single 2 in. diameter CARC panels were contaminated with 1000 $\mu g/cm^2$ (10 g/m^2) HD, which was spread evenly over the panel using a strip of Parafilm. HD was allowed to sit on the panel for 1 h prior to decontamination. One milliliter of decon solution was added and allowed to act for 15 min. Panels were then rinsed with water, dried briefly in air, and analyzed for HD. In cases where contact hazard assessments and extractions ($CHCl_3$) were performed, the amounts of HD were combined to provide the total HD remaining.
[b] Contact and extraction
[c] Extraction only
[d] Base formula: 0.1 M PAB and 0.5 M SPC in water
[e] Base formula: 0.1 M PAB and 0.8 M SPC in wate.

Table 5. Effect of Surfactant, Alone, on Decontamination of HD on CARC Painted Panels.[a]

Surfactant	Total HD Remaining ($\mu g/cm^2$)	% Decon
None[b]	239	76.1
1% Triton[®] X-405[b]	77	92.3
2% Triton[®] X-405[b]	82	91.8
5% Triton[®] X-405[b]	104	89.6
10% Triton[®] X-405[b]	68	93.2
20% Triton[®] X-405[b]	85	91.5

[a] Single 2 in. diameter CARC panels were contaminated with 1000 $\mu g/cm^2$ (10 g/m^2) HD, which was spread evenly over the panel using a strip of Parafilm. HD was allowed to sit on the panel for 1 h prior to decontamination. One milliliter of decon solution was added and allowed to act for 15 min. Panels were then rinsed with water, dried briefly in air, and analyzed for total HD by extraction ($CHCl_3$).
[b] Base formula: 0.1 M PAB in water.

Table 6. Effect of Triton® X-405 on the Decontamination of HD on CARC Painted Panels Using PD[a]

Decon	Total HD Remaining ($\mu g/cm^2$)	% Decon
1% Triton® X-405[b]	138	86.2
5% Triton® X-405[b]	105	89.5
10% Triton® X-405[b] (Run 1)	55	94.5
10% Triton® X-405[b] (Run 2)	163	83.7
15% Triton® X-405[b]	209	79.1
20% Triton® X-405[b]	170	83.0

[a]Single 2 in. diameter CARC panels were contaminated with 1000 $\mu g/cm^2$ (10 g/m^2) HD, which was spread evenly over the panel using a strip of Parafilm. HD was allowed to sit on the panel for 1 h prior to decontamination. Onemilliliter of decon solution was added and allowed to act for 15 min. Panels were then rinsed with water, dried briefly in air, and analyzed for total HD by extraction ($CHCl_3$).
[b]Base formula: 10% PD, 0.3 M K_2CO_3, 0.01 M K_2MoO_4, and 0.04 M citric acid in water.

Testing to optimize VX reactivity showed that the high pH required to completely react with 1:50 challenges tended to foam greatly, indicative of poor stability (pot-life). Attempts at reducing the pH, while increasing the amount of PD (as shown successful for SPC), found that solution viscosity increased greatly beyond about 15 wt% PD owing to thickening by the polyvinylpyrrolidinone constituent. Thus, this limits the reaction-capacity achievable for VX. GD challenges of 1:50, on the other hand, are easily decontaminated by such modest-pH, low-PD solutions.

2.5.4.2   Low Temperature Testing

Further testing for low-temperature compatibility showed that PAB/PD solutions with propylene glycol (PG) did not freeze, slush, nor precipitate down to at least -35 °C (-31 °F). For low-temperature use, it was envisioned that PG-water solutions can be provided along with the DCC as a "cold-weather kit". To improve surface penetration under subzero conditions, it was also decided to include 10% propylene carbonate into the cold-weather kit.

2.5.4.3   Bio Testing

PAB/PD decon formulation mixtures were tested* to assure their compatibility and efficacy for bio decontamination using *B. anthracis* and *B. subtilis* (stimulant) spores. In addition to PAB, for these studies, baseline formulation mixtures included the following.

    1.5 g PD
    1.0 g EC
    4.14 g PG
    0.024 g K_2MoO_4

*Wells, C.; Shegogue, D.; Delgado, J.; McPherson, D.; Hooban, C.; Sobota, A.; Sobota, L. *Single Tube Method (STM) for Testing the Decontamination Efficacy of a Peracetate Solvent Against B. Subtilis and B. Anthracis Δ Sterne Spores Inoculated on Large Coupons*; NSWCDD: Dahlgren, VA, unpublished data, May 2010.

0.083 g K$_2$CO$_3$
0.811 g Potassium Citrate Monohydrate
10 mL 5% TX-405 solution in water

2.5.4.3.1   Suspension Testing

Initial liquid suspension tests were used to determine the PAB concentration for use in subsequent testing (Section 2.5.4.3.2). As mentioned earlier (see Section 2.5.1.2), a PAB concentration of 20 mg/mL (0.04 M) was found adequate for complete kill of *B. anthracis* Δ Sterne spores. However, this testing was repeated for PAB/PD decon formula mixtures, using PAB concentrations of 40, 30, 20, 10, and 5 mg/mL (0 mg/mL PAB was used as a control) on *B. anthracis* Δ Sterne and *B.subtilis* (simulant) spores (Figures 2-3). The results show that 20 mg/mL PAB in PD decon formula mixtures still provided for total kill of both spore species. Thus, 20 mg/mL PAB was used in further testing and formulation work.

2.5.4.3.2   Bio Decon on Surfaces

Testing* employed the Single Tube Method (STM) for liquid decontamination, using surface swabs and wipes, to test PAB/PD decon solutions (with 20 mg/mL PAB) on larger material panels: glass, butyl rubber, polycarbonate, CARC, Air Force Top Coat (AFTC) paint, aluminum, and steel. Results for *B. anthracis* Δ Sterne and *B. subtilis* are shown in Figures 4 and 5. The results show that PAB/PD decon formulation are efficacious bio decontaminants on various surfaces but, as is typical, spores are harder to kill on surfaces than in suspension; thus, unlike suspension testing, complete kills are often not achieved.
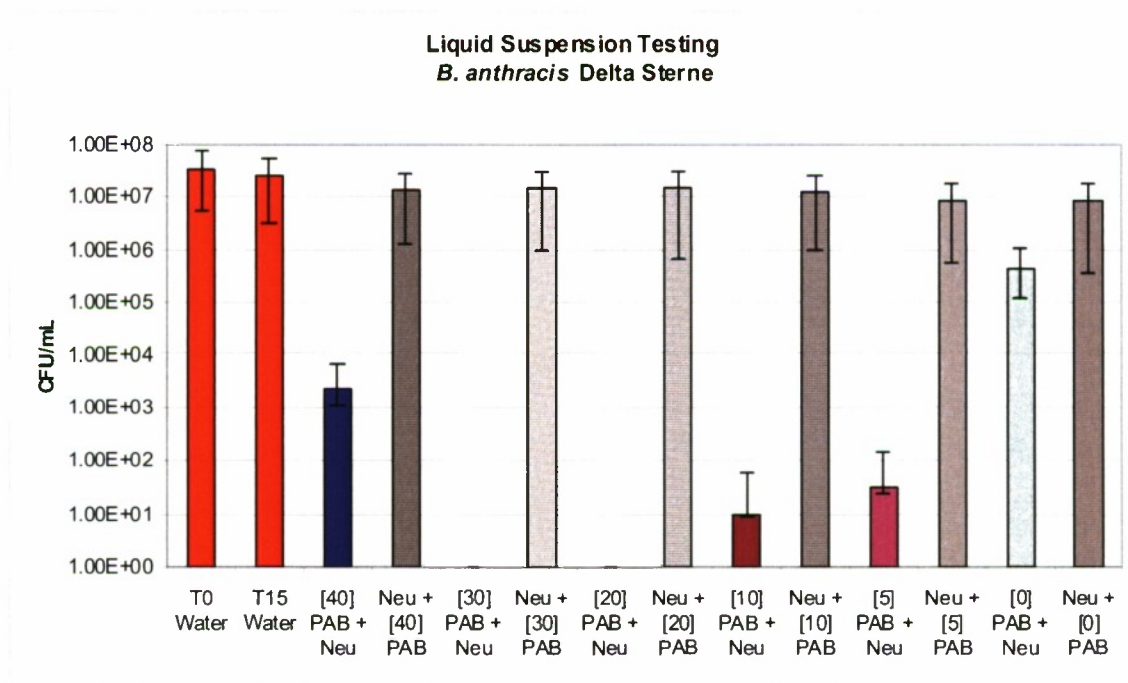
Figure 2. Bio Decon of *B. anthracis* Δ Sterne in Suspension using Indicated Amounts of PAB in PD Formulations

Liquid Suspension Testing
B. subtilis spores
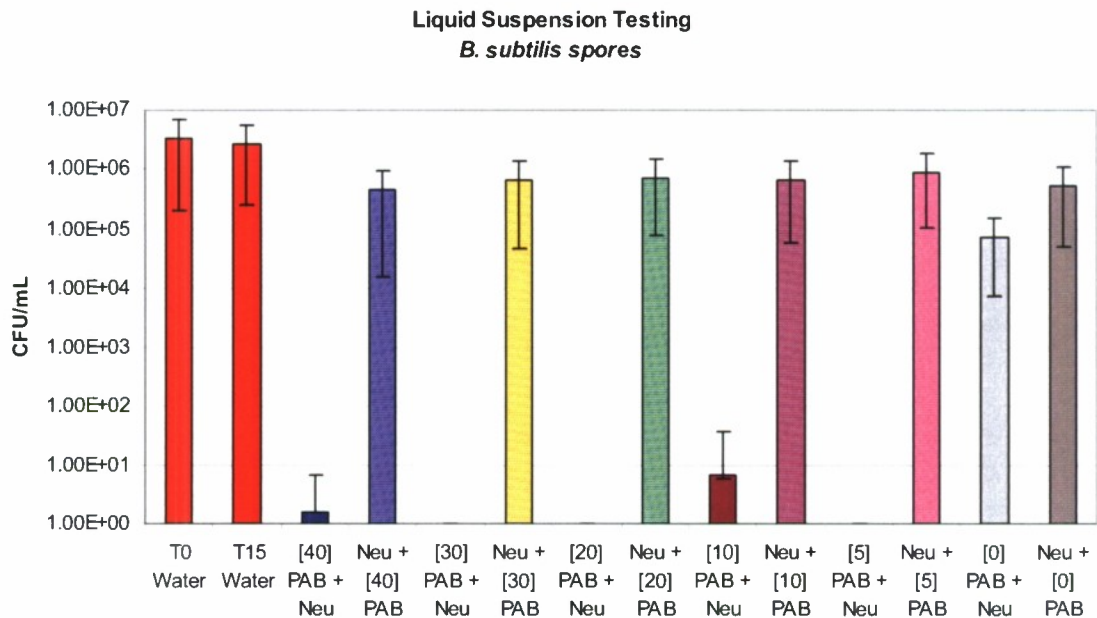
Figure 3. Bio Decon of *B. subtilis* in Suspension using Indicated Amounts of PAB

Large Coupon Decontamination Studies
B. anthracis **Delta Sterne spores**
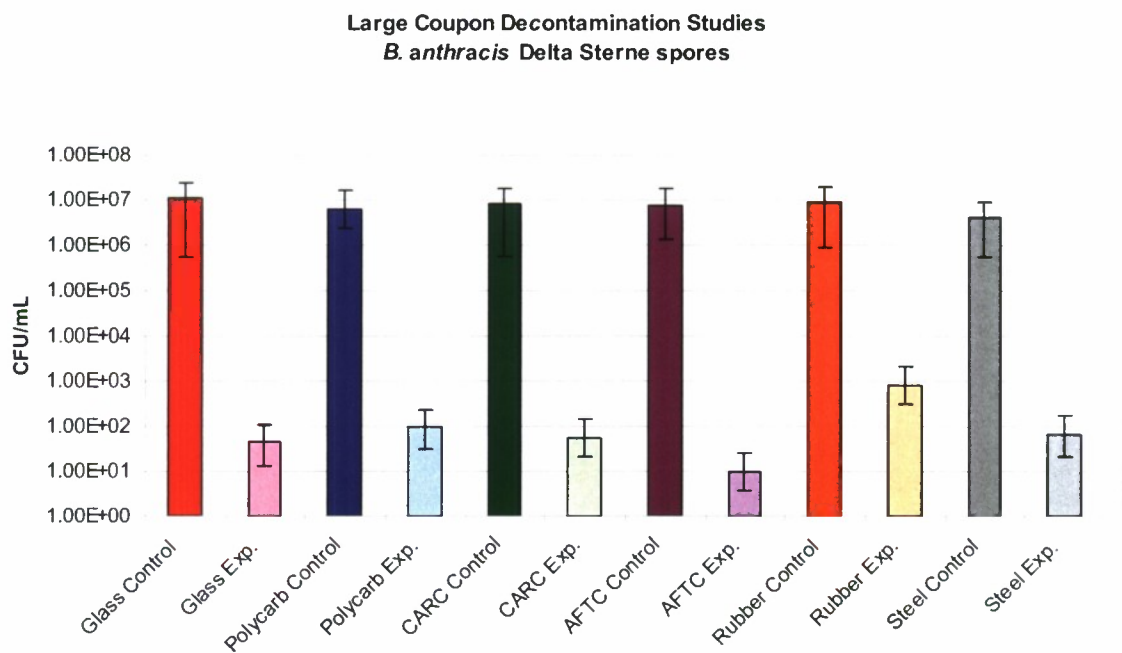
Figure 4. Efficacy of PAB/PD Decon Formulation on 10^7 Challenges of *B. anthracis* Δ Sterne using 15 min Application on Various Surfaces
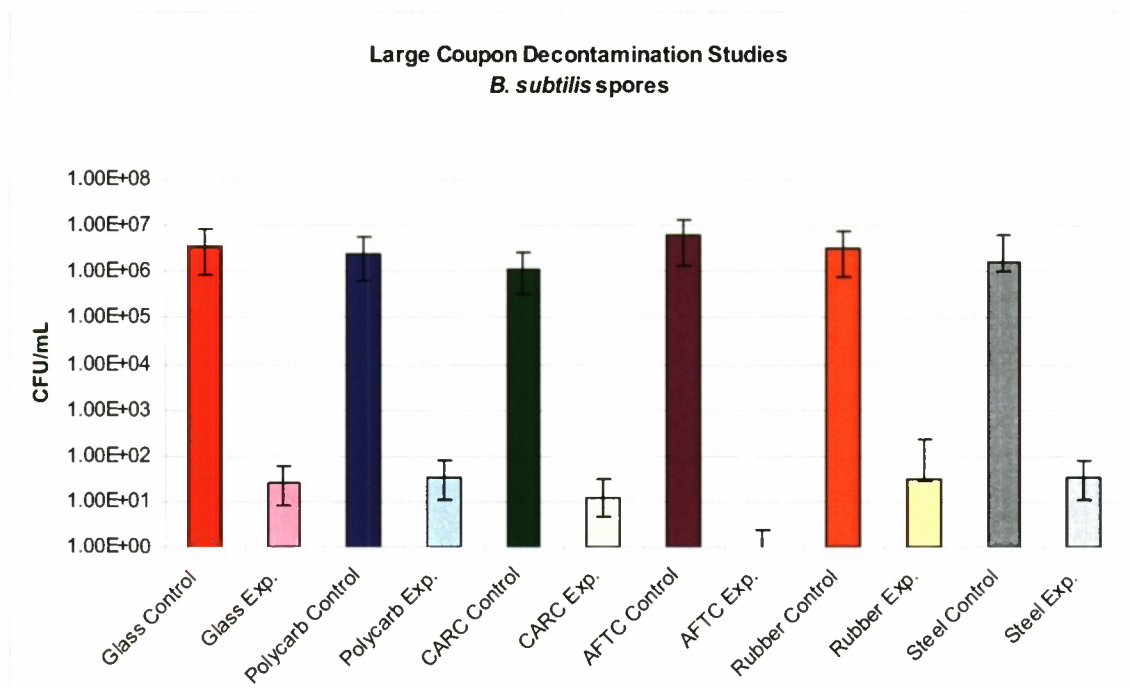
Figure 5. Efficacy of PAB/PD Decon Formulation on 10^7 Challenges of *B. subtilis* using 15 min Application on Various Surfaces

2.6   Final DDC Formula Testing

2.6.1   DDC Final Formula

Optimization of the DDC and cold-weather kit for low-temperature performance, batch stability at ambient temperature, and overall reactivity for VX, GD, and HD, arrived at the final formula shown in Table 7. This formula is divided into three parts according to the constituents' compatibilities. The amounts shown reflect the final concentration of each in the fully-mixed formula. The amounts of each constituent to make 1 L of the DCC are shown in parentheses.

Table 7. Dry Decon Concentrate Formula and Its Cold-Weather Kit

Part A PD	Part B PAB	Part C Activators/Buffers/Surfactant	Optional Cold-Weather Kit
15% PD (150 g)	0.04 M PAB (20.4 g)	0.225 M K_2CO_3 (31.1 g)	35% PG (350 mL)
		0.25 M Potassium Citrate Monohydrate (81.1 g)	10% PC (100 mL)
		0.01 M K_2MO_4 (2.38 g)	35% Water (350 mL)
		1% Triton® X-405 (10 g)	

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2.6.2   "DDC" Formulated with H_2O_2 Rather than PD

        Solid peroxygen compounds such as PD are thought to afford a savings with regard to the weight and/or logistical footprint of a formulated decontaminant. Yet, considering that the 15 wt% PD used in the DDC (Table 7) provides about 2.6 wt% H_2O_2, the same amount of H_2O_2 could be supplied by using only 7.4 wt% aqueous 35% H_2O_2—half the weight of the PD. Moreover, this amount of aqueous 35% H_2O_2 would also supply 4.8% of the water needed to reconstitute the DDC, affording a further, albeit slight, reduction in logistics. Finally, DDC formulated with aqueous H_2O_2, rather than PD and its associated polyvinylpyrrolidinone polymer constituent, would have a lower viscosity; perhaps improving surface penetration. Of course, besides mere weight of the DDC, other logistical factors need to be considered such as a preference for shipping powders rather than liquids to avoid potential leakage of the latter.

        To sort out any potential efficacy differences in PD versus less-viscous aqueous H_2O_2–formulated "DDC"—a composition for which PD is replaced with an equivalent amount of 35% H_2O_2—was also developed. Results for this variant at ambient temperature are discussed below. Also, low-temperature studies at – 32 °C are currently underway, examining its comparative efficacy with regard to normal DDC using simulants.

2.6.3   Chemical Agent Testing

2.6.3.1   Reactivity in Solution

        Agent reactions* with the DDC final formula at ambient temperature (not including the cold-weather kit constituents) in solution is shown in Table 8.

Table 8. VX, HD, and GD Reactions with DDC[20]

Time	VX	HD	GD
2 min	64.0%		Not Detected
5 min	38.8%	31.3%	
10 min	25.2%		
15 min	19.4%	15.0%	
30 min	10.8%	2.7%	
1 h	4.3%	Not Detected	
2 h	1.4%		
3 h	Not Detected		

        The reaction with GD is too fast to measure as it falls below detectable levels within 2 min. However, the reaction with VX is much slower, but it does proceed to completion within 3 h. HD reacts in intermediate fashion, falling below detectable limits within 1 h.

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*1:50 challenges of agent to decontaminant were used. HD reactions were rapidly stirred in glass vials, sampled, and analyzed by NMR.[7] VX and GD reactions were observed in situ by NMR.[7]

The reaction with HD was encouraged with vigorous, constant stirring, whereas (water-soluble) VX and GD reaction were merely initiated with a couple of quick shakes to afford their immediate dissolution. Thus, HD only dissolved/reacted with sufficient, sustained agitation. This is typical behavior when trying to dissolve oil in water containing minimum amounts of surfactant as in the present case. It should be noted, however, that decontaminants containing heavy solvent/surfactant content, such as Decon Green Classic® and, to a lesser extent, New Decon Green®, readily dissolve HD without vigorous stirring. This differing "ease-of-dissolution" for HD has direct impact on the ability of a decontaminant to decontaminate HD on surfaces as discussed in the next section.

2.6.3.2 Panel Tests

The primary surface of military interest is CARC paint and the most difficult agent to decontaminate, by far, is HD.[1] Thus, to prove the surface-decon efficacy of DDC, panel tests were conducted with HD on CARC. DDC and its less-viscous H_2O_2-variant (no PD) were examined. New Decon Green® and Decon Green® Classic were included for comparison as the latter has been shown to be more efficacious for agents on CARC paint than DS2.[1] Results are shown in Table 9.

Table 9. Decontamination of HD on CARC Surface[a]

Decon	Total HD Remaining ($\mu g/cm^2$)	% Decon
DDC	353	64.7
DDC, H_2O_2-Variant[b]	453	54.7
New Decon Green®	165	83.5
Decon Green® Classic	47	95.3
Required Operational Level	10	99.0

[a]Single 2 in. diameter CARC panels were contaminated with 1000 $\mu g/cm^2$ (10 g/m^2) HD, which was spread evenly over the panel using a strip of Parafilm. HD was allowed to sit on the panel for 1 h prior to decontamination. Onemilliliter of decon solution was added and allowed to act for 15 min. Panels were then rinsed with water, dried briefly in air, and analyzed for total HD by extraction ($CHCl_3$).
[b]Formulated with an equivalent amount of 35% H_2O_2 rather than PD

From these results it is clear that DDC, even though it is more viscous, is able to decontaminate HD on CARC paint just as well, if not better, than its less-viscous H_2O_2-variant. However, both do not perform as well as New Decon Green® and Decon Green® Classic owing to the better ability of these decontaminants to quickly dissolve HD without agitation. This is especially true for Decon Green® Classic. It not only contains the highest solvent-content but is also the only decontaminant which approaches the desired operational level of 10 $\mu g/cm^2$. Indeed, it perhaps even surpasses this mark since contact hazard levels tend to be quite a bit less than residual or extractable-amounts of agent on a surface.

2.6.3.3 What About Off-Gassing?

Besides assessing the efficacy of a decontaminant based on contact hazard, another assessment bandied about is off-gassing or vapor hazard (i.e., to what extent does a contaminated surface contaminate the air around it?).

ORD documents[6] specify the desired Vapor/Aerosol Levels for Nerve - G, Nerve - V, and Blister - H agents as reproduced in Table 10. The rationale behind this requirement is to "allow resources to be returned to operational use and reduce MOPP level required for personnel." With regard to the detection of agent on contaminated surfaces, the ORD further mentions the use of "detectors measuring from a distance of 1 in. from the surface..." Thus, it appears that vapor concentration quite close to the surface is of primary interest as this is where testing is to be done under real-world field-conditions.

Table 10. ORD Vapor/Aerosol Levels (mg/m^3)[6]

Level	Nerve - G	Nerve - V	Blister - H
Threshold (30 min, Cumulative)	<0.001	<0.001	<0.02
Objective (8 h, Time Weighted Average)	<0.0001	<0.00001	<0.0003

To rationalize exactly what a vapor concentration presumably emanating from a contaminated surface means, it is fortunate that the ORD mentions a measuring distance of 1 in from the surface. For example, one would not expect to find the same vapor concentration at distances of 1 in and 100 yards from the surface. So, the expected concentration very near the surface is of prime concern, with the understanding that it would tend to decrease as one gets further away.

At least for CARC surfaces, decontamination rarely, if ever,[1] results in contact levels below the those specified by ORD documents, which are shown in Table 11. Thus, these values serve as a useful starting point when considering off-gassing or vapor hazard from a contaminated surface.

It is easy to envision toxic vapor arising from a contaminated surface as depicted in Figure 6. For purposes of simplification, zero wind condition is assumed so that the "cloud" is symmetric.

Table 11. ORD Contact Exposure Levels (mg/m^2)[6]

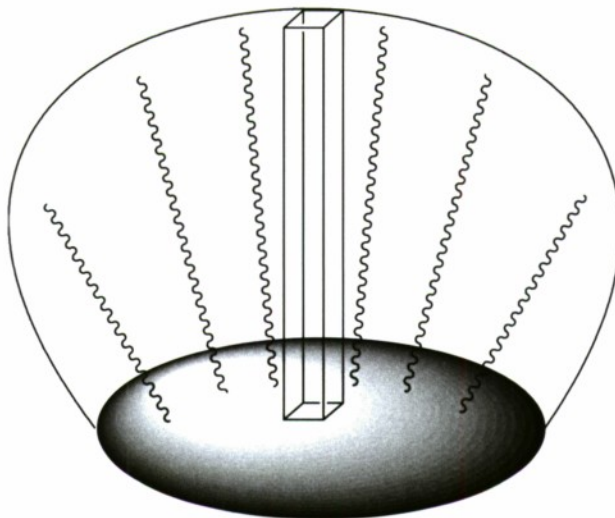|	Nerve - G	Nerve - V	Blister - H
Liquid Quantity	<16.7	<0.78	<100
Percent Neutralization	>99.8	>99.9	>99.0

Figure 6. Depiction of a Contaminated Surface Off-Gassing and the Associated
Vapor Cloud (zero-wind conditions)

Perhaps a particularly illustrative way to relate a known *surface* concentration hazard to an anticipated *vapor* concentration hazard is to consider a shaft of air over a unit area near the center of the contaminated area (to avoid edge-effects). The rectangular shaft rising from the square in Figure 6 shows the height to which the vapor concentration of a critical hazard level (Table 10) can be expected to rise. It really doesn't matter what the size of the deposit is or the size of the unit area (shaft) chosen because the surface concentration (Table 11) is defined per unit area and the shaft in question is surrounded by identical shafts (so edge-effects on central shafts can be ignored).

The contact and vapor hazard values in Tables 10 and 11 are expressed in mg/m^3 and mg/m^2, respectively. This is the convenient unit to use when considering larger items, anywhere from a vehicle to a contaminated urban area. Yet, it is more convenient for small items such as a rifle or for laboratory testing of small panels (see above) to represent the contact hazard data in $\mu g/cm^2$. However, as previously mentioned, the actual dimension considered is irrelevant. The height to which a particular surface concentration of agent is able to fill a shaft of 1 m × 1 m dimension is the same for a 1 cm × 1 cm shaft. Sample calculations for GD (the worst case) are shown in Table 12 for the Contact Exposure Levels quoted in   Table 11 and the Threshold Vapor Levels given in Table 10. Illustration of the relative heights to which the vapor hazard is theoretically possible to rise over larger deposits is shown in   Figure 7. Note that vertical dimensions of the shafts in the figure (in feet) are not to scale with the base (in meters).

Table 12. Sample Calculations for the Height to which the GD Threshold Vapor Hazard Concentration Can Rise from a Surface Possessing the GD ORD Contact Exposure Level

	Shaft Dimension	
	1 m × 1 m	1 cm × 1 cm
Amount of GD contained on shaft base	16.7 mg	1.67 µg
Volume of air required to yield vapor concentration of 0.001 mg/m^3	16.7 mg ÷ 0.001 mg/m^3 = 16,700 m^3	1.67 µg ÷ 0.001 mg/m^3 × (1 mg/1000 µg) = 1.67 m^3
Height of shaft required to accommodate volume of vapor hazard (V ÷ A = H)	16,700 m^3 ÷ 1 m^2 = 16,700 m or 54,900' *	1.67 m^3 ÷ 1 cm^2 × (100 cm/m)^2 = 1,6700 m

* 5280' = 1 mile = 1.609 km

It is clear from Figure 7 that at threshold contact hazard levels, the potential vapor hazard levels for each agent extend quite far from the surface. GD, for example, extends upward beyond the typical flight levels (FL) of passenger jets. And the situation is even more absurd if the Objective Vapor Levels are considered: In this instance, GD would rise to 167 km, albeit still comfortably below the space station (360 km). Thus, it is quite obvious from Figure 7 that at a height of 1 in. above the surface, vapor hazard levels resulting from the minimum contact hazard levels should be quite enormous.

Even though small items would not generate the outrageous plumes associated with large vehicles or contaminated wide areas (Figure 7), they can still contaminate quite large volumes of air when taken into vehicles, aircraft, buildings, etc. For example, the interior of the C-141 cargo plane shown in Figure 7 is about 1000 m^2. Exceeding the threshold vapor hazard concentration for GD of 0.001 mg/m^3 within this aircraft would require just a *single item less than the size of a small book* contaminated at the GD contact hazard level of 16.7 mg/m^2 being brought on board (an item possessing an area of about 600 cm^2). So, similar arguments regarding the futility of bothering to measure vapor hazards when the known contact hazard is in far excess of the ORDs apply to small items as well. Such items are still able to contaminate large volumes of air within their vicinity or when brought into confined areas.

As previously mentioned, detectable contact levels for the agents typically are in excess of the threshold contact levels following the decontamination of CARC paint. The values found for HD on CARC in the current study are certainly no exception. Therefore, time and resources were not expended to actually measure these lofty vapor hazard levels. With the low decon efficiencies afforded by CARC paint,[1] it is sufficient to say that any off-gassing agent concentrations would be very high compared to even threshold ORD Vapor Levels–sky high.

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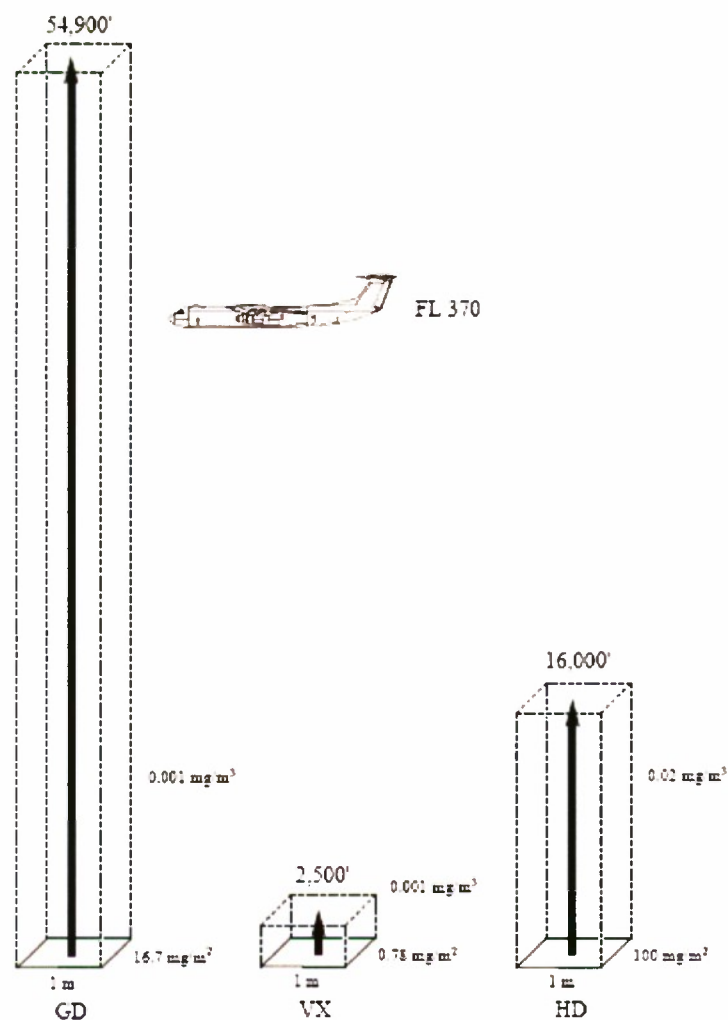
Figure 7. Depiction of the Height of the Potential ORD Threshold Vapor Contamination Levels (mg/m^3) Arising from a Surface with a Known ORD Contact Hazard Contamination Level (mg/m^2) for GD, VX, and HD

2.6.4   Materials Testing

Materials testing was conducted for DDC, including the cold-weather kit, with aluminum, steel, CARC, AFTC, polycarbonate, nylon, JSGPM mask sheet material, and CP Type II 14 mil butyl rubber gloves, using 24 h immersion followed by 4 h drying.

2.6.4.1   Metals

Results for aluminum and steel are shown in Table 13. Water was used as a control. Excellent ratings were obtained for both of these metals. Pictures taken of the test coupons are shown in Figure 8. Note that for steel, the panels appear more rusty following treatment with water than with DDC.

Table 13. Exposure of Aluminum and Steel to DDC/Cold-Weather Kit for 24 h[*]

Coupon Material	Mass Change (g)	Coupon Area (cm2)	Corrosion Rate (mils/y)	Result
Aluminum Type 5052 Decon	-0.00141693	39.56	1.942	EXCELLENT
Aluminum Type 5052 Water	-0.00026680	40.21	0.360	EXCELLENT
Carbon Steel AISI 1020 Decon	-0.00083933	39.30	0.395	EXCELLENT
Carbon Steel AISI 1020 Water	-0.00413000	39.25	1.947	EXCELLENT

[*] Criteria: <2 mils/y excellent; 2-10 mils/y good; 10-20 mils/y fair; 20-50 mils/y poor; >50 mils/y failure

Figure 8. Aluminum and Steel Coupons Following 24 h Exposure to
DDC/Cold-Weather Kit and Water (control)

2.6.4.2   Paints

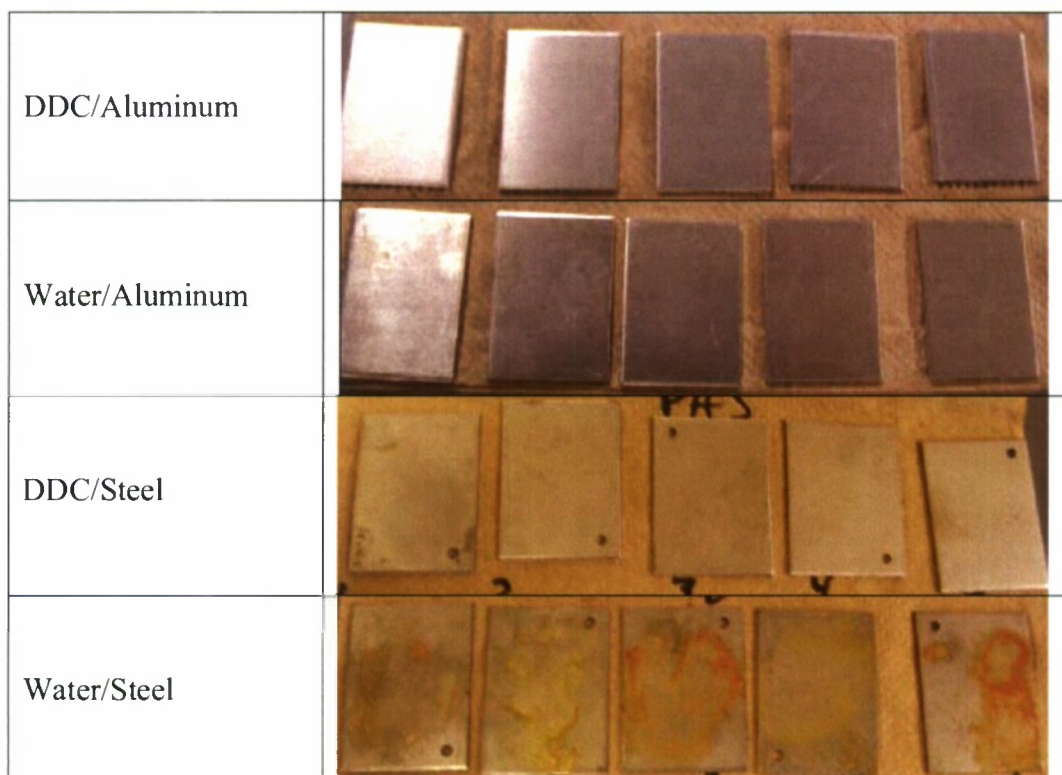Results for CARC and Air Force Top Coat (AFTC) paints following 24 h soak in DDC/Cold-Weather Kit are given in Table 14. Water was used as a control. Both paints passed the test, in terms of maintaining thickness and hardness.

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Table 14. Effect of DDC/Cold-Weather Kit on Paints*

Coupon Material	Coating Thickness			Coating Hardness Data			
	Thickness Change (um)	% Change	Result	Initial Pencil Class	Post-exposure Pencil Class	Pencil Class Change	Result
Water Based CARC Decon	0.936	1.0%	PASS	8H	8H	No change	PASS
Water Based CARC Water	-0.208	-0.2%	PASS	8H	8H	No change	PASS
AFTC Decon	0.66	0.8%	PASS	8H	8H	No change	PASS
AFTC Water	2.244	3.8%	PASS	8H	8H	No change	PASS

*Criteria: thickness, <20% Pass; hardness, <2 pencil class change

2.6.4.3   Plastics and Individual Protective Equipment (IPE)

Results for plastic and IPE materials exposed to DDS/Cold-Weather Kit for 24 h are shown in Tables 15 and 16. Water was used as a control. All materials passed. Of particular note, the Humvee Light Housing (polycarbonate) was severely weakened and damaged by Decon Green® Classic[3] but not by the either reformulated New Decon Green® or DDC/Cold-Weather Kit. This is attributable to the very high propylene carbonate content of the former (55%), whereas the latter decontaminants only contain 10% of this solvent. Also, polycarbonate mask lens material is hazed by Decon Green® Classic[3] but not New Decon Green® or DDC/Cold-Weather Kit; again, because of their lower solvent content. With regard to the failures exhibited by butyl rubber and nylon for water, the results appear to be a matter of experimental error.

Table 15. Effect of DDC/Cold-Weather Kit on Plastics and IPE*

Coupon Material	Sorption Data			Durometer Hardness Data		
	Mass Change (g)	% Change	Result	Durometer Change	% Change	Result
JSGPM Sheet Material Decon	0.01263	0.30%	PASS	0.59	1.0%	PASS
JSGPM Sheet Material Water	0.00532	0.12%	PASS	0.72	1.2%	PASS
14 mil Butyl Rubber Glove Decon	0.00112	0.13%	PASS	0.81	1.0%	PASS
14 mil Butyl Rubber Glove Water	0.00091	0.11%	PASS	2.12	2.6%	FAIL
Nylon Decon	0.01773	0.27%	PASS	-1.28	-1.6%	PASS
Nylon Water	0.03703	0.56%	PASS	-2.56	-3.2%	FAIL
Humvee Light Housing Decon	0.01136	0.15%	PASS	1.18	1.9%	PASS
Humvee Light Housing Water	0.00897	0.12%	PASS	0.32	0.5%	PASS

*Criteria: mass change <5% Pass; hardness change <2% pass

Table 16. Effect of DDC/Cold-Weather Kit on Plastics and IPE (Mask Lens)[*]

Coupon Material	Sorption Data			Haze and Transmittance Data					
	Mass Change (g)	% Change	Result	Haze Change	% Change	Result	Transmittance Change	% Change	Result
Polycarbonate Decon	0.00339	0.07%	PASS	0.515	59%	PASS	-0.147	-0.17%	PASS
Polycarbonate Water	0.00305	0.06%	PASS	0.417	63%	PASS	-0.113	-0.13%	PASS

[*]Criteria: haze change <500% pass; transmittance change <1% pass

2.6.4.4 Other Decontaminants

Assessments were conducted* of the compatibility of DDC/Cold-Weather Kit with other decontaminants: RSDL, aqueous HTH, and DF200. Two scenarios were tested: adding a foreign decontaminant to the mixed DDC and adding mixed DDC to solid HTH mixed in a sand-shuffle pit. The results are shown in Figure 9 and Table 17.

A temperature rise of 16.6 °C or greater is potentially unsafe, indicating that an incompatibility exists. The largest and fastest temperature rise occurred when 10% aqueous HTH was mixed with the DDC/Cold-Weather Kit and excessive foaming ensued. It is known that chlorine decomposes H_2O_2, and these observations are attributed to this phenomenon. It should be noted that similar behavior with HTH would be exhibited by Decon Green® and DF200, as both of these contaminants contain H_2O_2. No untoward behavior occurred between DDC and DF200. A slight temperature rise occurred for RSDL, and a thick precipitate occurred when 75% RSDL was mixed with DDC (but not for lower concentrations of 25 and 50% RSDL). However, in practice, a 75% RSDL mixture with DDC is rather unlikely to occur because RSDL comes in only small packets for personal use (skin decon); thus, large quantities should not exist in the field. Although none of the decontaminants effected temperature rises >16.6 °C when mixed with DDC, the decontaminant is considered compatible with the liquid decontaminants RSDL, 10% aqueous HTH, and DF200 but not with solid HTH (see below).

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*Wells, C.; Crowley, K.; Hooban, C.; Dean, J.; Owens, T. *Petroleum, Oils, Lubricants (POLS), Materials, and Chemical Compatibility Testing for the Peracetate Solvent Decontaminant*; NSWC: Dahlgren, VA; unpublished data, May 2010.

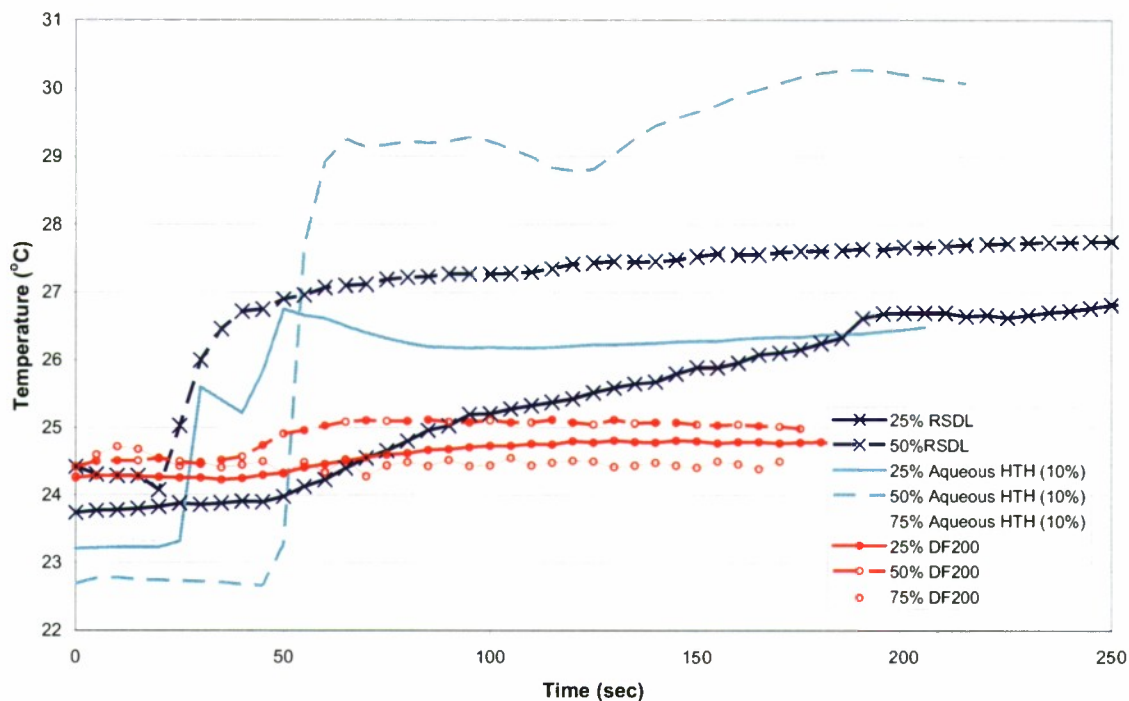**Peracetate Solvent Chemical Compatibility Testing**

Figure 9. Temperature Rises Observed by the Addition of Various Volumes of RSDL,
Aqueous HTH, and DF200 to DDC/Cold-Weather Kit

Table 17. Observed Temperature Rises for the Addition of Decontaminants to
DDC/Cold-Weather Kit

Decon Added	10% HTH in water		DF200		RSDL	
Mass % Added	Temp Rise (°C)	Maximum Rate of Rise (°C/s)	Temp Rise (°C)	Maximum Rate of Rise (°C/s)	Temp Rise (°C)	Maximum Rate of Rise (°C/s)
25%	3.54	0.46	0.55	0.016	3.98	0.058
50%	7.58	0.88	0.7	0.034	3.81	0.19
75%	5.27	0.66	0.45	0.066	-	-

Whereas 10% aqueous HTH exhibited acceptable heating, the addition of 15 mL DDC/Cold-Weather Kit to 5 g of (solid) HTH/Sand shuffle pit mixture resulted in a 19.4 °C temperature rise over the course of 500 s (Figure 10). A small amount of foaming was also observed consistent with H_2O_2 decomposition. The observed temperature rise is in excess of the

16.6 °C criteria for thermal chemical incompatibility set for this test. Thus, DDC is judged not compatible with HTH/Sand shuffle pit mixtures.
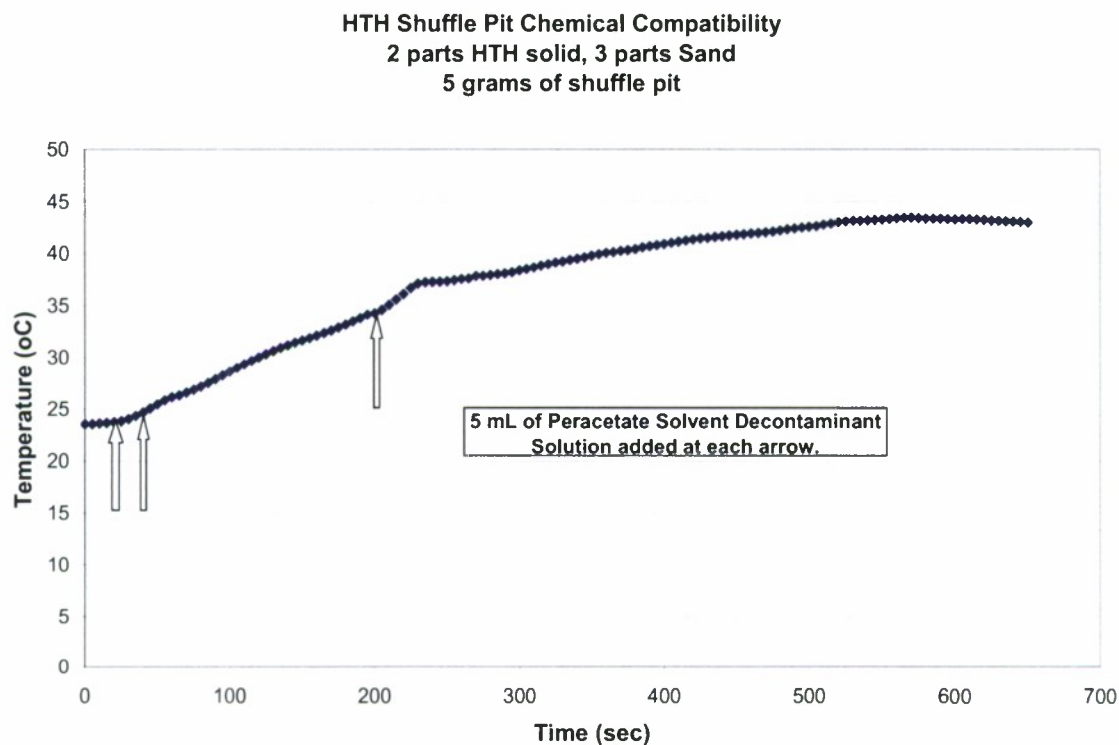
HTH Shuffle Pit Chemical Compatibility
2 parts HTH solid, 3 parts Sand
5 grams of shuffle pit

Figure 10. Temperature Rise Noted for Addition of DDC/Cold-Weather Kit to HTH/Sand Shuffle Pit Mixture

2.6.4.5   Compatibility with Petroleums, Oils, and Lubricants (POLs)

Figure 11 shows temperature changes associated with mixing DDC/Cold-Weather Kit with petroleums, oils, and lubricants (POLs).* There is no significant temperature increase with any POL and there was no evidence of any reaction. Therefore, DDC is presumably compatible with POLs under normal conditions.

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*Wells, C.; Crowley, K.; Hooban, C.; Dean, J.; Owens, T. *Petroleum, Oils, Lubricants (POLS), Materials, and Chemical Compatibility Testing for the Peracetate Solvent Decontaminant*; NSWC: Dahlgren, VA; unpublished data, May 2010.

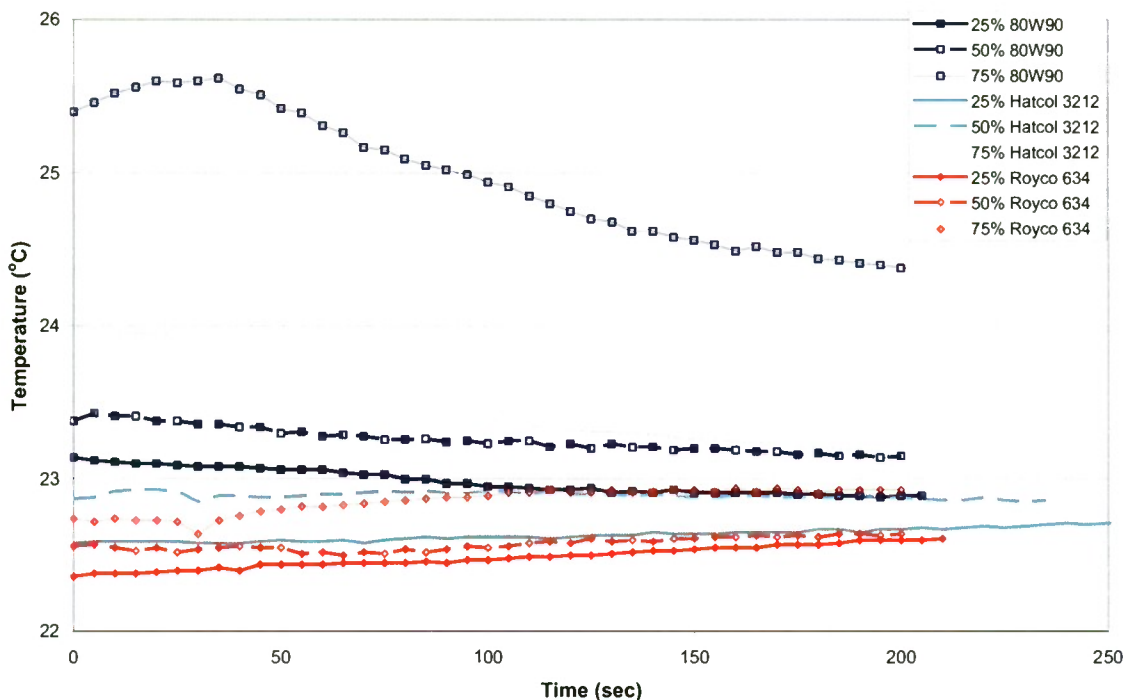## Peracetate Solvent POLs Chemical Compatibility Testing

Figure 11. Observed Temperature Changes for DDC/Cold-Weather Kit Mixed
with POLs

2.6.5   Comments on Radiological/Nuclear Decontamination Efficacy of DDC

Previous studies conducted by Lumetta et al.[20] with New Decon Green® to determine efficacy for removal of radioactive isotopes from various surfaces associated with vehicles (glass, aluminum, steel, CARC, rubber) showed remarkable efficacy for ^{60}Co on recalcitrant materials such as steel, aluminum, and rubber (Table 18). Citrate and bicarbonate anions are known chelators; thus, the radioisotope-removal efficacy exhibited by Decon Green® is reasonably attributable to these ingredients. DDS contains these same chelator and it is anticipated that DDS will similarly provide for Rad/Nuc isotope removal, although testing is need for verification.

Table 18. Efficacy of New Decon Green® for Radiological Isotope Removal[20]

Sample Set	% Removal of Co or Cs From:				
	Aluminum	Al/CARC	Glass	Rubber	Steel
^{60}Co DECON GREEN®	97.1±1.7	85.3±1.7	100.0±0.0	97.2±0.4	48.1±5.7
^{60}Co H$_2$O Control	85.8±7.3	88.9±3.4	99.9±0.0	66.7±4.1	7.7±3.2
^{137}Cs DECON GREEN®	99.8±0.1	97.6±0.1	100.0±0.0	99.9±0.0	99.2±0.1
^{137}Cs H$_2$O Control	99.8±0.0	99.8±0.0	99.9±0.0	99.9±0.1	99.0±0.3

2.7   Conclusions

The all-solid dry decon concentrate (DDC) developed under this project is an efficacious, broad-spectrum CB decontaminant, requiring only water for reconstitution and use at ambient temperatures. For subzero use, an optional Cold-Weather Kit may be used to provide performance down to -32 °C (-26 °F). Further, because of its citrate and bicarbonate activators, the DDC should also provide enhanced capability for radiological/nuclear (RN) decon as well. DDC is completely compatible with aluminum, steel, Chemical Agent Resistant Coating (CARC), Air Force Top Coat (AFTC), and individual protective equipment (IPE). It is also compatible with petroleum, oils, and lubricants (POLs) under normal conditions. Finally, DDC is compatible with other decontaminants such as RSDL, DF200, and 10% aqueous HTH, but not with solid HTH/Sand "shuffle pit" mixtures as excessive heating can occur with the latter decontaminant.

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